Non-Polluting Replacement for Chromate Conversion coating & Zinc Phosphating in Powder Coating Applications.

MR. DAVID FERGUSON

U.S. ENVIRONMENTAL PROTECTION AGENCY

National Risk Management Research Laboratory

Office of Research and Development, Cincinnati, OH 45268

DR. BRUCE MONZYK

Battelle, 505 King Avenue, Columbus, OH 43201-2693

Abstract

Picklex®, a proprietary formulation, is an alternative to conventional metal surface pretreatments. Its developers claim that it does not produce waste or lower production rates, and it will maintain performance compared to conventional processes. A laboratory program was designed to compare Picklex® with conventional processes in common, large scale, pollution surface finishing operations. This was done using steel and aluminum panels, measuring product coating properties, process operability, and costs. A total of 41 different combinations of substrate, degreaser, pretreatment, conversion coat, and powder coat were tested in which qualities such as finish adhesion, bending adhesion, impact adhesion, hardness, and corrosion resistance were evaluated. Results indicate that Picklex®-pretreated panels performed as well as panels that were conventionally pretreated, and with a simpler non-hazardous process. Picklex® is particularly acceptable for powder coated steel or aluminum, replacing chromate conversion coating for aluminum substrates and zinc phosphating for steel substrates. This paper gives results from an actual field study in a power coating shop and validates the lab results. An engineering assessment indicated that Picklex® can have cost advantages as well.

Acknowledgements

EPA and Battelle would like to thank Brian Mills, Vice President of Operations at Mills Metal Finishing, personally, and Mills Metal Finishing corporately for their cooperation and assistance during the field testing as well as communications throughout the process.

EPA and Battelle also acknowledges the valuable contributions by an anonymous manufacturing company who is identified as Commercial Partner No. 1 in this report. They provided commercial components, powder coat resin, and their test results and evaluation.

Acronyms and Abbreviations

aq	aqueous solutions
ASTM	American Society for Testing and Materials
CC	conversion coating
CrCC	chromate conversion coating
CFR	Code of Federal Regulations
DI	de-ionized
EC	electro-cleaning
ENi	electroless nickel (plating)
HCr	Hard Chromium
ICP	International Chemical Products, Inc.
IWTP	Industrial Waste Treatment Plant
MSDS	material safety data sheets
NA	not applicable
NRMRL	National Risk Management Research Laboratory
PEC	purchased equipment cost
ppm	parts per million (weight/weight)
QA	quality assurance
QC	quality control
SEM	scanning electron microscope/microscopy
TCLP	Toxicity Characteristic Leaching Procedure
TOC	total organic carbon
U.S. EPA	United States Environmental Protection Agency
UV	ultraviolet
ZnP	Zinc phosphatizing (all variations)

Objectives

The overall objective of this study was to evaluate the ability of Picklex® as a metal pretreatment or pretreatment/conversion coat in finishing operations which can be used to eliminate or reduce the amount of hazardous and toxic chemicals. This objective must be accomplished while maintaining equal or better product performance properties, with economic benefit or no significant economic penalty. Reduction in waste produced would be accomplished through the elimination of processing steps, and hence, the waste stream volumes from these steps, especially those processes involving ventilation of warm or gassing solutions. These improvements are expected to decrease production costs. The cost of Picklex® raw material would offset these savings somewhat. The specific objective was to evaluate Picklex® applications for powder coating finishes on aluminum and steel through representative commercial field tests. The evaluation focused on technical performance and economics while validating the previous laboratory tests and environmental benefits.[Ferguson]

Background

Metal surface finishing is a major manufacturing industry consisting of thousands of production shops that provide weather- and wear-resistant and/or aesthetically pleasing manufactured products. The volume of hazardous/toxic waste streams produced from metal surface finishing operations is significant (U.S. EPA, 1995). It is common for product surfaces to undergo more than 10 finishing steps that include degreasing and cleaning (for oil removal and de-scaling), etching, de-smuting, pickling, plating, and rinsing. The elimination of any of the surface processing steps is desired by manufactures to reduce processing costs, waste production, and energy consumption. With this objective in mind, a no-waste surface-finishing agent designed to provide a nearly one-step metal surface preparation operation for metal finishing operations would be of great benefit.

In this study, Picklex® provides metal surface cleaning, pickling, conversion coating, and priming using a process simply consisting of degreasing, one dip-step (can also be sprayed), one rinse, and then final process. For powder coating field tests, oven drying occurred after the one dip-step. Because many surface-finishing operations exist, the potential for sizable waste and cost reductions by using Picklex® are significant. Therefore, the National Risk Management Research Laboratory (NRMRL) of the United States Environmental Protection Agency (U.S. EPA) contracted Battelle to perform a joint assessment of the efficacy of Picklex® in major polluting surface-finishing operations. This paper summarizes these findings.

Field Testing

Field-produced components and panels similar to those used in Phase I testing were evaluated at a commercial metal surface treatment vendor using their equipment and personnel. These test components and panels after treatment and powder coating were then evaluated with the same coating performance test conducted in Phase I.

A focused field test with Picklex® for powder coating applications on aluminum and steel was studied. A total of 41 different combinations of substrate, degreaser, pretreatment, conversion coat, and powder coat were tested. Only panels and components, with little to no visible corrosion products, were used. Aluminum 3105 and low carbon steel 1010 panels were used. Also aluminum die cast alloy and malleable iron casting components were processed.

Three batches of panels and/or components were processed at Mills Metal Finishing. The first batch included steel and aluminum panels and served as a process validation from the laboratory to industrial setting. The second batch included commercial components and panels. The third batch included both components and panels and focused on using Spraylat PE6639M, which is the Commercial Partner's standard powder coat material used on the aluminum components for production use.

The coatings were evaluated by a matrix of tests including adhesion, bend adhesion, impact adhesion, hardness, and corrosion resistance. Results indicate that the field testing replicated the laboratory processes performed during Phase I[(Ferguson)]. Picklex® may serve as a degreaser for steel. The Picklex® processing time can be reduced relative to the laboratory tests and conventional surface preparation processes. The immersion time for aluminum can be decreased from 5 minutes to 30 seconds. Eliminating rinsing after Picklex® was found to produce undesirable results and insufficient adherence of powder coating to substrate.

Picklex® as a Pretreatment

The field testing replicated the results of the laboratory processes. The field testing showed slightly better results for Picklex® than conventional surface-finishing processes for bend and impact adhesion. In general, Table 3 compares results between the two phases for conventionally pretreated panels versus Picklex® pretreated panels.

Picklex® may serve as a degreaser for steel. During Batch No. 2, one group of steel panels was processed through Picklex® without a conversion coat and skipping the degreasing step. This group produced performance results similar to those processed with Picklex® and no conversion coat, but with the degreasing included. Further testing is recommended to show replication of these results, especially with lightly pre-greased feed material.

During Phase II, the immersion time was reduced from 5 minutes to 30 seconds for aluminum and from 5 minutes to 90 seconds for steel. Table 4 shows a comparison between Batch Nos. 1 and 2 for commercial degreaser, Picklex® (with varying times), and 45-second rinses. Depending on the corrosion resistance needed for the application, shorter Picklex® immersion times might be acceptable. The 5-minute immersion time gives greater corrosion resistance than the 90-second application. The corrosion resistance on aluminum was equivalent for all other test parameters.

Table 3. Comparison of Coating Performance Results of Conventionally Pretreated Panels versus Picklex® Pretreated Panels – Phase I & Phase II

Coating	Phase	Tape Adhesion	Bend	Impact Adhesion	Corrosion Resistance
China White Powder Topcoat on Aluminum	Phase I	Equivalent[a]	Equivalent[a] passed, while CCC Picklex® conventional cracked with no peeling/flaking	Equivalent[a]	Equivalent[a]
	Phase II	Equivalent[a]	Equivalent[a] passed	Picklex® CCC slightly better, conventional CCC had one failure	Equivalent[a]
China White Powder Topcoat on Steel	Phase I	Equivalent[a]	Equivalent[a] passed, cracking with Picklex® and conventional	Conventional slightly better than Picklex®	Equivalent®
	Phase II	Equivalent[a]	Equivalent[a] passed	Equivalent[a]	Equivalent[a]

(a) Conventional and Picklex® pretreated panels provided the same coating performance.
(b) Panels processed in Picklex® for 5 minutes and rinsed in DI water for 45 seconds before receiving conversion coat.

Table 4. Effect of Picklex® Process Time

Powder Coating	Process Time	Tape Adhesion	Bend	Impact Adhesion	Corrosion Resistance
China White Powder Topcoat on Aluminum	5 vs. 0.5 min.	Equivalent[a]	Equivalent[a]	Equivalent[a] passed with 5 minute application receiving slightly higher readings	Equivalent[a]
China White Powder Topcoat on Steel	5 vs. 1.5 min.	Equivalent[a]	Equivalent[a]	Equivalent[a] passed with 5 minute application receiving slightly higher readings	Depending on application needs, 5 minute application has higher corrosion resistance than 90 second application

(a) Differences in Picklex® processing time provided the same coating performance.
(b) Both rinses were at 45 sec and conversion coating step was skipped.

The vendor recommended eliminating the rinse after processing with Picklex® for powder topcoats. The field testing on panels showed that for aluminum and steel at least a quick rinse (in and out) is needed. For the non-rinsed case, the aluminum and steel surfaces appeared to be very tacky with inconsistent residual Picklex® deposit remaining after drying. This residual Picklex® did not allow the powder coat to adhere properly causing failures. For example, one group of steel panels in Batch No. 2 failed in the salt fog chamber much sooner than the group with a rinse after Picklex®.

Surface–Finishing Procedures

Three different degreasing conditions were used for the field testing. Certain panels in Batch No. 1 were degreased with toluene at Battelle before processing further to replicate the Phase I laboratory test results. At Mills, certain non-degreased panels were degreased with Zep I.D. Red, and certain other sets of panels were not degreased

Two pretreatment systems were used for each type of material: commercial pretreatment and Picklex® pretreatment. For aluminum, the pretreatment consisted of Mills' normal process line, a soak cleaner, two rinses, an etch, two rinses, a deoxidizer, and two rinses. For steel, each commercial pretreatment consisted of Mills' normal process line, a cleaner and then a series of rinses. For Picklex® pretreatment, Picklex® was used for a specified time and then one rinse was performed at a specified time if at all as per the test sequence. In both cases a conversion coat was followed unless this step was skipped and the Picklex® served as the conversion coat also. The two commercial conversion coatings which were reviewed during field testing are chromate for aluminum and zinc phosphate for steel. All of the components and panels completely processed at Mills were powder coated. Figure 1 illustrates the process steps for both conventional zinc phosphatizing on steel and the Picklex® process. The use of Picklex® replaces the pretreatment (electro cleaner and one rinse step) and conversion coating (conversion coat and three rinses). Figure 2 illustrates the sequential process steps for both conventional chromate conversion coating on aluminum and the alternative Picklex® process. As shown, the use of Picklex® (Al-P-R-N-N-PC) replaces both the pretreatment (alkali cleaning, 2 rinse steps, etch, 3 rinse steps, deoxidizer, 2 rinse steps) and chromate conversion coating (chromate conversion coat and three rinse steps).

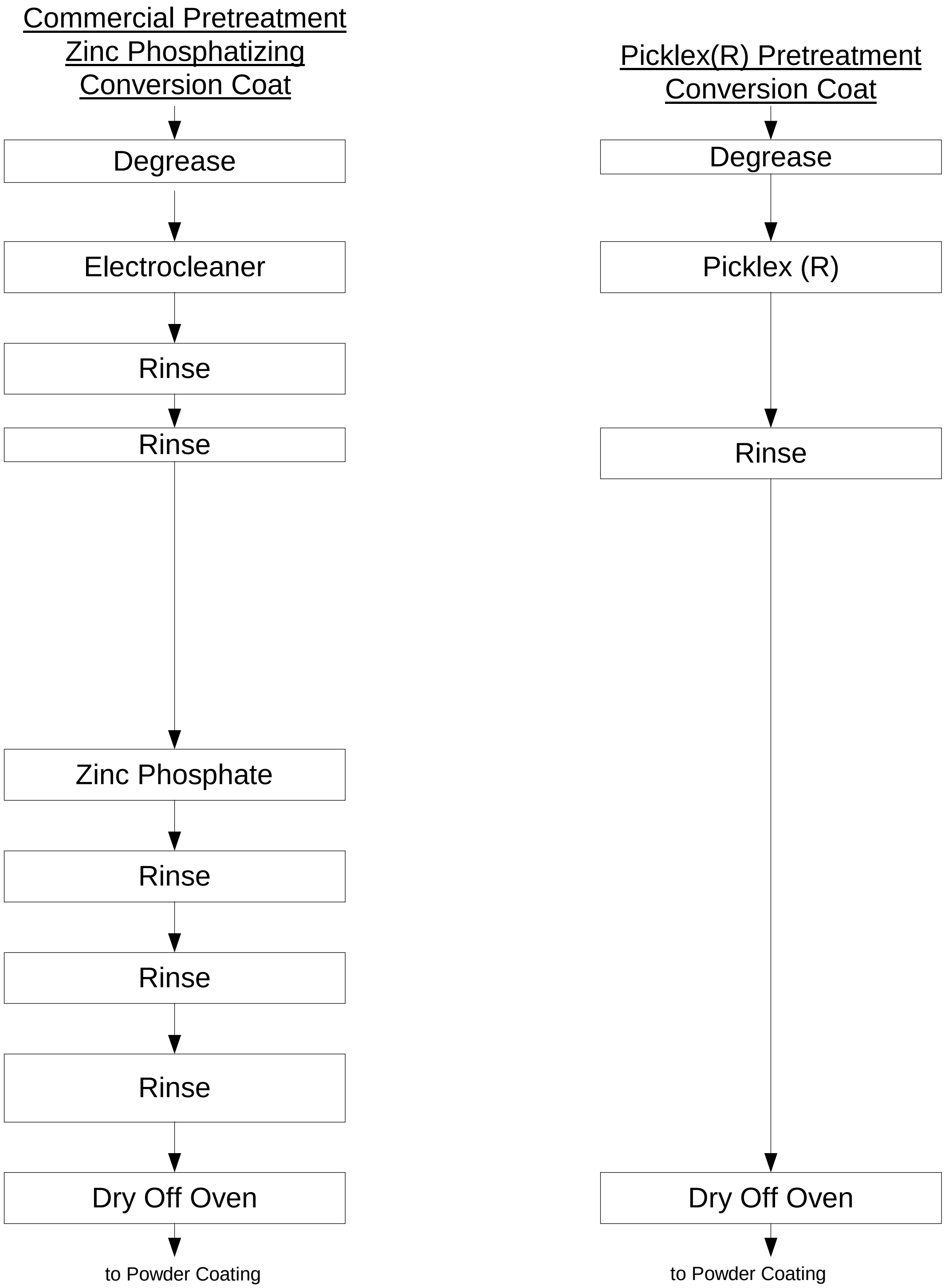

Figure 1. Processes for Commercial Pretreatment Zinc Phosphate Conversion and Picklex® Pretreatment Conversion Coatings on Steel

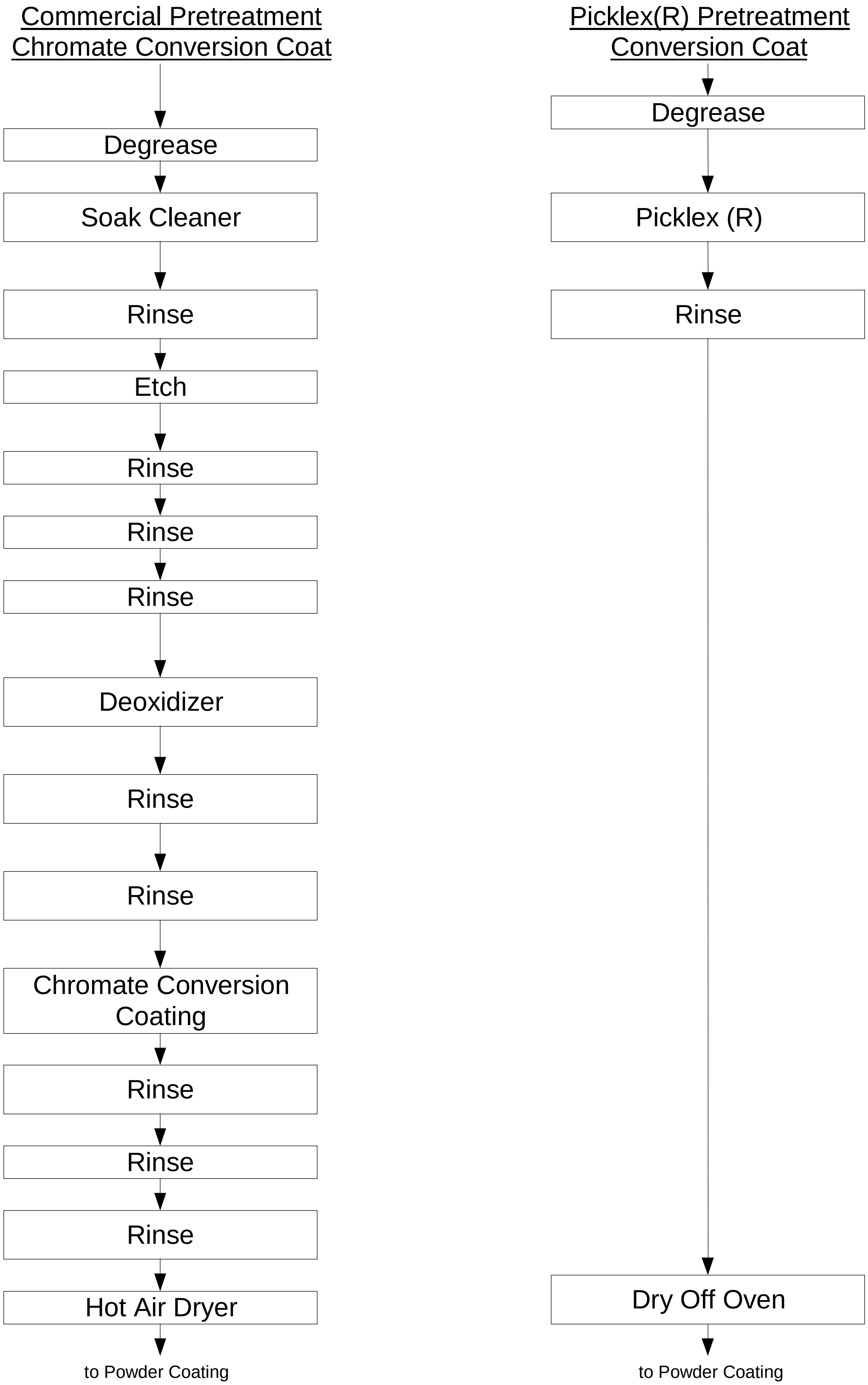

Figure 2. Processes for Commercial Pretreatment Chromate Conversion and Picklex® Pretreatment Conversion Coatings on Aluminum

Test Panels

Following Phase I protocol metal test panels were obtained from Q-Panel Laboratory Products (Cleveland, OH).[(1)] Surface treatments were applied to aluminum 3105 and steel 1010 because the two alloys were tested in Phase I and represent large commercial usage. A minimum of two panels was used for each surface finish evaluation parameter

Figure 3. Powder Coating Operation

Three powder coatings were used to coat test panels in the field trials, Vista SH-2004 china white from Ferro Powder Coatings Division and PE6639M and PEB1867C from Spraylat Corporation. China white powder coat material, which was obtained and used during Phase I, was used for all batches in Phase II to replicate the powder coat material used during Phase I. Two Spraylat products supplied by the Commercial Partner No. l, Spraylat PEB1867C and PE6639M, were also used in Phase II. The Spraylat PEB1867C was used for Batch Nos. 1 and 2. Spraylat PE6639M, was used for Batch No. 3. The Spraylat PE6639M was applied to Batch No. 3, aluminum panels and components because this powder coat material is the standard material for the Commercial Partner No. 1's die cast aluminum parts

Technical Performance

This section summarizes the technical performance evaluation by the various coating performance parameters and addresses the economic and overall feasibility issues in engineering assessment.

Powder Coating Film Thickness

Dry powder-coating film thickness was measured on coated panels by ASTM D 1186 and ASTM D 1400, averaging six readings for each panel. Table 5 shows the thickness range for Batch Nos. 1, 2, and 3 compared with the manufacturer's recommendations for applied thickness.

Table 5. Dry Film Thickness of Powder Coatings on Test Substrates

Batch	**Substrate**	**Powder Coating**	**Thickness Range (mils)**	**Target Thickness (mils)**
BATCH No. 1	Steel	China White	1.65 to 2.88	2.0±1.0
	Aluminum	PEB1867C	1.24 to 2.14	2.0 ±1.0
	Aluminum	China White	1.24 to 2.24	2.0 ±1.0
BATCH No. 2	Steel	China White	0.93 to 1.74	2.0±1.0
	Aluminum	China White	1.14 to 2.29	2.0±1.0
	Aluminum	PEB1867C	1.03 to 1.99	2.0±1.0
BATCH No. 3	Steel	China White	2.88 to 3.29	3.0±1.0
	Aluminum	PE6639M	2.74 to 3.39	3.0±1.0

Adhesion by Tape Test

Adhesion by tape was determined by ASTM D 3359. The ratings can be summarized as:

- 5B The edges of the cuts are completely smooth; none of the squares of the lattice is detached.
- 4B Small flakes of the coating are detached at intersections; less than 5% of the area is affected.
- 3B Small flakes of the coating are detached along edges and at intersections of cuts. The area affected is 5 to 15% of the lattice.
- 2B The coating has flaked along the edges and on parts of the squares. The area affected is 15 to 35% of the lattice.
- 1B The coating has flaked along the edges of cuts in large ribbons and whole squares have detached. The area affected is 35 to 65% of the lattice.
- 0B Flaking and detachment was worse than Grade 1B.

Table 6 lists the adhesion by tape ranges for each group of panels. All of the steel panels coated with China White and tested for adhesion by tape were rated 5B except one panel. In Batch No. 3 panel GGG16 was rated 4B for adhesion by tape.

Adhesion by tape results for aluminum panels coated with PEB1867C in Batch No. 1 and Batch No. 2 were rated 5B. Aluminum panels coated with China White in Batch No. 1 were rated 5B except one panel (Z22), which was rated 4B. In Batch No. 3 the aluminum panels were coated with PE6639M and adhesion by tape ratings include one panel at 2B, one panel at 3B, and four panels at 4B. Adhesion for Batch No. 3 aluminum panels is not as good as panels coated in earlier batches. Adhesion could be less for the PE6639M coating than the others, or there may be environmental process, or operator differences during the third batch of processing and coating relative to the first two batches.

In Batch No. 1 and Batch No. 2, adhesion by tape did not reveal any discernible differences between the different treatment scenarios. Batch No. 1 Group A, conventional pretreatment and chromate conversion coat; Group B, Picklex® pretreatment and chromate conversion coat; Group J, conventional pretreatment and zinc phosphate conversion coat; and Group K, Picklex® pretreatment and zinc phosphate conversion coat, served as a replication for the processes used during Phase I. Table 1 shows equivalent results between the two different processes compared to those from Phase I. Supporting the use of Picklex® as a degreaser for steel, group CC from Batch No. 2, which was not degreased, achieved the same tape adhesion results as group BB from Batch No. 2, which was the exact same process plus the degreasing step. Tape adhesion results for certain groups showed that the Picklex® immersion time can be reduced from 5 minutes to 30 seconds for aluminum and 90 seconds for steel. The aluminum groups were the following for aluminum: group F from Batch No. 1, with a 5 minute immersion time and group S from Batch No. 2, with a 30 second immersion time. The steel groups were the following: group M from Batch No. 2, with a 5 minute immersion time and group BB with a 90 second immersion time.

Test System Designation

Each test system was identified by a combination of 9 abbreviations that referenced the substrate material, the degreaser, the pretreatment system, the rinse after pretreatment, the water break test, the conversion coating, the rinse after conversion coating, the dryer, and the powder coat material. The abbreviation code used in the report is shown on Table 6.

Table 6. Summary of Results from Materials Testing

Batch	Group	Test ID[a]	Dry Film Thickness Range	Adhesion by Tape Range	Impact Adhesion: Average Impact (foot – pounds)	Impact Adhesion: Sample I.D. of Failures	Sample I.D. of Bend Adhesion Failures	Salt Fog: Exposure Time (hours)	Salt Fog: Adhesion by Tape Range[c]	Salt Fog: Creepage Range[d]
Aluminum										
1	A	Al-T-C-R-n-Cr-R-A-CW	1.27-1.89	5B	40	6		1760	5B	
1	B	Al-T-P5M-R-w-Cr-R-A-CW	1.91-2.24	5B	54			1760	5B	
1	C	Al-T-P5M-R-w-N-N-O-CW	1.85-2.18	5B	59			1760	4B	
1	D	Al-C-C-R-n-Cr-R-A-CW	1.86-2.07	5B	64			1760	5B	
1	E	Al-C-P5M-R-w-Cr-R-A-CW	1.93-2.57	5B	65			1760	4B	
1	F	Al-C-P5M-R-w-N-N-O-CW	2.04-2.68	5B	66			1760	3-4B	
1	G	Al-T-P5M-R-w-Cr-R-A-SB	1.63-2.04	5B	4	13, 10, 3, 18	12	1760	5B	
1	H	Al-C-P5M-R-w-Cr-R-A-SB	1.24-1.83	5B	4	11, 2, 8, 18		1760	5B	
1	I	Al-C-P5M-R-w-N-N-O-SB	1.85-2.14	5B	4	1, 4, 10, 17		1760	3-4B	
2	Q	Al-C-P30S-R-w-Cr-R-A-CW	1.23-2.28	5B	60			1277	5B	
2	R	Al-C-P30S-N-w-N-N-O-SB	1.42-1.77	5B	4	6, 19, 26, 35	3,14,31	1277	3-4B	
2	S	Al-C-P30S-R-w-N-N-O-CW	1.39-1.55	5B	46			1277	4B	
2	T	Al-C-P30S-R-w-N-N-O-SB	1.08-1.58	5B	4	2, 13, 27, 34	5,23,31	1277	5B	
2	U	Al-C-C-R-w-Cr-R-A-CW	1.14-1.30	5B	60			1277	5B	
2	V	Al-C-C-R-w-Cr-R-A-SB	1.29-1.99	5B	4	1, 15, 24, 36	5,22,31	1277	5B	
2	X	Al-C-P30S-R-w-Cr-R-A-SB	1.05-1.42	5B	5		2,9,22	1277	5B	
2	Y	Al-C-P30S-N-w-N-N-O-CW	1.53-2.29	5B	4	8, 17, 25, 29	3,9,32	1277	2-4B	
2	Z	Al-C-P30S-N-w-N-N-O-CW	1.31-1.77	4-5B	4	9, 13, 26, 27	3,16,32	1277	0-2B	
2	RR	Al-C-P30S-QR-w-N-N-O-SB	1.03-1.38	5B	4	1, 6, 8, 11	3,7,10	1277	2-4B	
2	SS	Al-C-P30S-QR-w-N-N-O-CW	1.35-1.82	5B	52			1277	4B	
3	AAA	Al-C-P30S-R-w-Cr-R-A-SA	2.88-3.39	2-4B	27		NA[e]	NA		
3	BBB	Al-C-P30S-R-w-N-N-O-SA	2.75-2.96	3-4B	35		NA	NA		
3	CCC	Al-C-P30S-QR-w-N-N-O-SA	2.74-3.00	4B	37		NA	NA		

Table 6. Summary of Results from Materials Testing

Batch	Group	Test ID[(a)]	Dry Film Thickness Range	Adhesion by Tape Range	Impact Adhesion: Average Impact (foot – pounds)	Impact Adhesion: Sample I.D. of Failures	Sample I.D. of Bend Adhesion Failures	Salt Fog: Exposure Time (hours)	Salt Fog: Adhesion by Tape Range[(c)]	Salt Fog: Creepage Range[(d)]
Steel										
1	J	Fe-T-C-R-w-ZnP-R-O-CW	1.95-2.0	5B	20			1760, J2 @1376		7 for J2
1	K	Fe-T-P5M-R-w-ZnP-R-O-CW	1.65-2.20	5B	25			1760		
1	L	Fe-T-P5M-R-n-N-N-O-CW	2.13-2.35	5B	160			1376		6
1	M	Fe-N-P5M-R-w-N-N-O-CW	2.14-2.88	5B	160			1376		5-6
1	N	Fe-C-C-R-w-ZnP-R-O-CW	1.88-2.11	5B	7	8,18		1376		6-7
1	O	Fe-C-P5M-R-w-ZnP-R-O-CW	1.68-2.82	5B	32			1760		
1	P	Fe-C-P5M-R-n-N-N-O-CW	2.04-2.40	5B	18			1376		5-6
2	AA	Fe-C-P90S-R-w-ZnP-R-O-CW	0.93-1.34	5B	4	25	21,32,34	893, AA16 @ 608		7-8
2	BB	Fe-C-P90S-R-w-N-N-O-CW	1.22-1.74	5B	155			893		5-6
2	CC	Fe-N-P90S-R-w-N-N-O-CW	1.46-1.58	5B	158			893		4-5
2	DD	Fe-C-P90S-N-w-N-N-O-CW	1.11-1.22	5B	160		22	608		3-4
2	EE	Fe-C-C-R-w-ZnP-R-O-CW	1.22-1.69	5B	26		7,16,20	893		6-7
3	GGG	Fe-C-P90S-N-w-N-N-O-CW	2.88-3.29	4-5B	30			(b)		

(a) First abbreviation is basis metal: Al=aluminum panel, Fe=steel panel, AlC=Aluminum component, FeC=steel component
Second abbreviation is degreaser: T=toluene, C=Mill's degreaser, N=No degrease step
Third abbreviation is pretreatment system: C=conventional (Mill's pretreatment), P5M=Picklex® for 5 minutes, P30S=Picklex® for 30 seconds, P90S=Picklex® for 90 seconds
Fourth abbreviation is rinse step after pretreatment system: R=rinse, N=no rinse step after pretreatment
Fifth abbreviation is water break step: W=water break test, N=no water break test to be performed
Sixth abbreviation is conversion coating system: Cr=chromate, ZnP=zinc phosphate, N=none
Seventh abbreviation is rinse after conversion coating system: R=rinse, N=none
Eighth abbreviation is drying system: O=dry off oven, A=hot air dry off box
Ninth abbreviation is powder coating system: CW=china white, SA=standard powder coat material for aluminum Spraylat PE6639M used during Batch 3, SB=Spraylat PEB1867C used during batches 1 and 2
NA=not applicable
(b) Sample still in salt fog chamber.
(c) Adhesion by Tape test performed after salt fog exposure.
(d) Creepage rating performed only on steel panels which had loss of coating adhesion on scribe.
(e) NA = not applicable, test not performed

Superior results were obtained when comparing adhesion of Commercial Partner No. 1's production parts versus Picklex® processed parts. Commercial Partner No. 1 provided 12 aluminum components for Batch No. 3 testing to be processed with Picklex®, and finished with the standard powder coat material for aluminum, Spraylat PE6639M. Upon receipt of processed components, Commercial Partner No. 1 measured for paint thickness and adhesion by tape following the ASTM D 3359. See Table 7 for adhesion by tape results. The adhesion by tape results were superior for all three variations using Picklex® compared to production samples from Commercial Partner No. 1. Further testing is recommended to validate these results on a production scale.

Table 7. Comparison of Commercial Partner No. 1's Production Samples versus Picklex® Treated Samples[3]

Sample Type	Adhesion Rating
Production Samples from Commercial Partner No. 1	0B-2B
DDD Picklex® Rinse (45 sec) Chromate Conversion Coating	4B
EEE Picklex® Rinse (45 sec)	3B-4B[a]
FFF Picklex® Quick Rinse	4B

(a) Only one sample received 3B rating. The remaining samples received 4B rating.

Pencil Hardness

ASTM D3363 *Standard Test Method for Film Hardness by Pencil Test* describes a procedure for rapid, inexpensive determination of the film hardness of an organic coating on a substrate. It was used here as a quality control check much like dry film thickness. The powder coatings used in this study were in the hardness range of HB to 3H with no discernable differences from substrate to substrate or scenario to scenario. This supports the hardness being a function of the coating itself and not the surface preparation or test substrate.

Impact

Impact was another way to evaluate adhesion of a coating to a substrate. The field testing replicated the laboratory tests through processing and evaluating groups A and B of Batch No. 1 for aluminum and J and K of Batch No. 1 for steel (all defined in adhesion by tape section). Phase II achieved additional promising results than Phase I for both aluminum and steel. For Aluminum, Phase I found impact adhesion between conventionally pretreated panels and Picklex® pretreated panels to be equivalent. Table 6 shows the average impact results for each group and the panels, which failed impact adhesion. Group A had one failure, A6, showing that Picklex® pretreated panels have slightly higher impact resistance than conventionally pretreated panels for aluminum. Impact resistance also showed that Picklex® can serve as at least a mild degreaser for steel, comparing group BB's average of 155 to group CC's similar average of 158 (both groups are defined in adhesion by tape section). Also, the comparison between F and S for aluminum and M and BB for steel show that the results are consistent.

Certain groups of aluminum panels from Batch No. 1 and 2 failed the impact adhesion test at 4 foot-pounds. All of the groups that were powder coated with Spraylat PEB1867C, which is not the standard powder coat material for aluminum, failed the test except for Group X which received very low passing results. These results suggest that the powder coat material and not the pretreatment or conversion coating caused the failures. Also groups Y and Z which did not receive a rinse after Picklex® failed the impact adhesion test at 4 foot-pounds. These results show that at least a quick rinse is needed after processing in Picklex®.

Bend

The mandrel bend test was provided as another way to evaluate adhesion of a coating to a substrate. Results for bend tests for Batch Nos. 1, 2, and 3 are listed in Table 6. In Phase II, pretreatment rather than top coating was being investigated; therefore, ASTM D 522 was modified in the definition of pass/ fail. In this study, visible cracking was not a “fail” unless coating was removed by pressure-sensitive tape at the cracking site. Failure was defined as loss of coating adhesion.

In Batch No. 1, only one aluminum panel, G12, failed this test while two panels with identical process steps passed. G12 (Al-T-P5M-R-w-Cr-R-A-SB) was powder coated with Spraylat PEB1867C, which is not the standard powder coat material for aluminum. All panels from Group B (Al-T-P5M-R-w-Cr-R-A-CW) passed the bend adhesion test. The only difference between Group G and Group B’s test sequences were the different powder coat material demonstrating that G12 most likely failed because of the powder coat material and not the pretreatment or conversion coating. Certain groups of aluminum panels from Batch No. 2; Groups V, X, and RR; were powder coated with Spraylat PEB1867C and failed the bend adhesion test. These results also support the powder coating material causing the bend adhesion failures.

The overall results for bend adhesion demonstrate that Picklex® can be used as both a pretreatment and conversion coat for steel and the processing time in Picklex® can be reduced to 90 seconds. In Batch No. 2, steel panels having zinc phosphate conversion coating, Groups AA and EE, failed the bend test. Steel panels, from groups BB and CC, processed in Picklex® for 90 seconds, rinsed in DI water for 45 seconds, dried, and then powder coated (skipping zinc phosphate conversion coating) passed the bend adhesion test. These results demonstrate that zinc phosphate conversion coating is not needed to achieve passing bend adhesion results for steel. In Batch No. 1, all steel panels passed the bend adhesion test. Comparing groups AA and EE to Group O from Batch No. 1, the only difference is that the Picklex® process time was reduced from 5 minutes in Batch No. 1 to 90 seconds in Batch No. 2. Both groups received zinc phosphate conversion coating. The bend adhesion results show when applying a zinc phosphate conversion coating, the process time in Picklex® needs to be greater than 90 seconds.

The field test (Phase II) bend results for groups A versus B (aluminum panels) and groups J versus K (steel panels) verify the results from previous laboratory test (Phase I) when comparing conventionally pretreated panels to Picklex® pretreated panels. This result demonstrates that equivalent results were obtained between the two tests. The bend results for group CC (no degreasing step on steel panels) compared to group BB (panels were degreased) give equivalent passing results and show superior results over the conventionally processed panels in Batch No.

2. The equivalent results between the two groups are another indication that Picklex® can serve as a degreaser for steel. Group DD had one failure, which showed cracking during the bend test demonstrating the need for steel to be rinsed after processing with Picklex® and before powder coating. Group GGG, Figure 4, is a replicate of group DD. Note the inconsistent surface. Groups Y and Z, aluminum panels that were processed in Picklex® and not rinsed before drying also failed the bend test. These results also support the need for a rinse after Picklex®.

Figure 4. Oven Dried Steel Panels with No Rinse after Picklex®

Corrosion

Corrosion testing used exposure in a salt fog chamber following ASTM B 117, Standard Practice for Operating Salt Spray Apparatus. Powder coated panels were scribed with an X, protected by tape on the edges, and exposed in a standard salt spray cabinet for periods up to 1760 hours. All panels were inspected at 200 hours for signs of corrosion and returned to the salt spray cabinet for continued exposure. Table 6 shows the results. Length of salt fog exposure was determined by time of processing and project end date. Batch No. 1 test panels were observed to 1760 hours. Batch No. 2 test panels were observed to 1277 hours. Batch No. 3 panels were observed to 144 hours. The failure point was defined for this study as loss of adhesion. Pressure-sensitive tape was placed over the scribed area on the dried panel and removed. If coating was removed with the tape, the panel failed.

Aluminum panels from Batch Nos. 1, 2, and 3 did not display loss of adhesion due to corrosion within the time frame of this study. Steel panels from Batch No. 1 did not show loss of adhesion until 1376 hours compared with similar panels from Batch No. 2, which showed loss of adhesion by 608 hours.

Comparing groups A versus B and J versus K (all groups from Batch No. 1), the salt fog results show that the laboratory process test results were verified in the field. During Phase I and II, equivalent corrosion resistance was noted when comparing commercially pretreated panels versus Picklex® pretreated panels. In Phase II Batch No. 1, both A and B groups of panels showed no corrosion at 1760 hours yielding equivalent corrosion resistance for aluminum also. For steel, both conventionally pretreated and Picklex® pretreated panels had corrosion on scribe and no undercut noted at 1760 hours when the samples were removed. One panel, J2, had loss of coating adhesion on scribe at 1376 hours and was removed. China White's process specification states corrosion resistance for 1000 hours. Group CC, in which Picklex® also replaced degreasing, showed the same amount of corrosion resistance as group BB, which was degreased, with loss of coating adhesion on scribe at 893 hours and sample was pulled from test.

The equivalent level of corrosion resistance is another factor in favor of using Picklex® as the degreaser for steel. When comparing group BB to M, it is found that higher corrosion resistance is achieved with a longer immersion time for Picklex® on steel, 893 hours for 90-second immersion versus 1376 hours for 5 minute immersion. For aluminum, the same amount of corrosion resistance was achieved when the immersion time was decreased shown by comparing Group F and S. Both groups of aluminum panels remained in the salt fog chamber for the duration of the test, 1760 and 1277 hours, respectively.

Batch No. 1 aluminum panels were pulled from the salt fog chamber at 1760 hours with no corrosion noted. Batch No. 2 aluminum panels were pulled from the salt fog chamber at 893 hours with no corrosion noted. After the salt fog test samples were removed from the exposure cabinet, the aluminum samples which showed no corrosion were tested for adhesion by tape to reveal possible loss of adhesion in the corrosive environment. Most of the aluminum panels retained high adhesion values of 5B and 4B equivalent to initial adhesion by tape values. Groups which were processed with Picklex® serving as the pretreatment and conversion coat, rinsed at least with a quick rinse, dried, and then powder coated with china white received at least a 4B rating. Two sets showed significant loss of adhesion. Z (Al-C-P3OS-N-w-N-N-O-CW) and Y (Al-C-P30S-N-w-N-N-O-CW) had panels receiving the lowest adhesion by tape ratings ranging from 0B to 2B. Both groups Y and Z were <u>not rinsed</u> before drying. This suggests that at least a quick rinse is needed after processing aluminum panels through Picklex® before drying them. Figure 5 shows panel Z 25 which received a 0B rating.

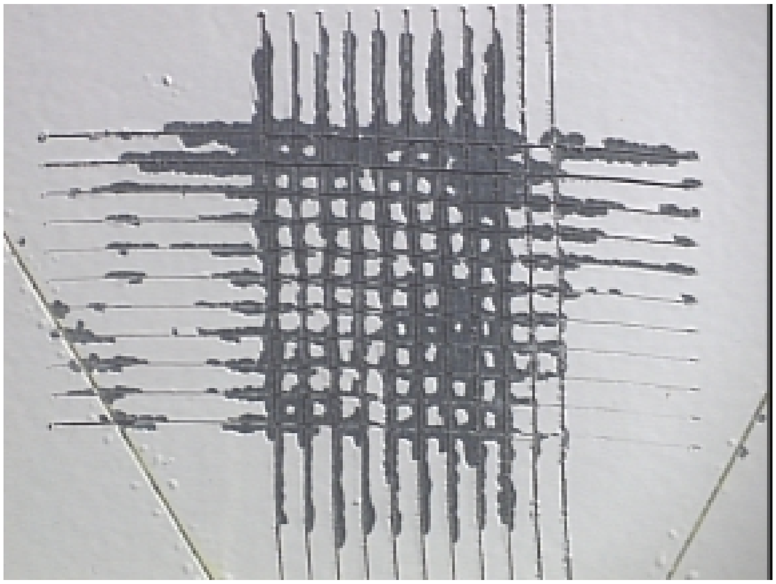

Figure 5. Panel Z 25 after Adhesion by Tape after Salt Fog Exposure

Engineering Assessment

Each Picklex® application was evaluated for the economic impact and cost advantages relative to the conventional processes in parallel to the laboratory testing provided above. Both the engineering design information and the economic evaluation are preliminary to guide subsequent Picklex® test program development and application priority, and especially, to address the most significant cost elements.

The objective of this assessment is to evaluate a preliminary engineering design and economics to guide the subsequent development and potential commercial implementation. Both capital and operating costs are estimated as incremental costs relative to the conventional processes. The capital cost estimates are order of magnitude and include 50% contingency because of the limited design detail available and the uncertainties of a general evaluation rather than site and application specific. A more detailed evaluation using site specific economic data will improve the accuracy and significance of the results in the future. Based on the commercial operation information obtained at Mills the engineering assessment has been revised to include commercial practice and potential labor savings. Several assumptions are included about consumption, make-up, and waste disposal rates that need to be verified during the technology development to produce a comprehensive evaluation.

A preliminary engineering assessment for each of the following surface-finishing applications are evaluated below relative to the Picklex® process based on the available test data.

- Chromate conversion coating on aluminum
- Zinc phosphatizing on steel.

Design Basis

A standard 500-gallon tank (36 inches by 72 inches by 48 inches) was used for all process steps to accommodate an assumed size piece to be handled. This simplified the preliminary design assessment and economics while recognizing that some operations may require different capacities and production rates to be addressed in subsequent iterations of the Engineering Assessment.

The following assumptions were used in this evaluation:

1. Metal surface treatment shop operates 8 hours per day and 5 days per week for 2,080 hours per year.
2. The use of Picklex® does not require changing the composition or operation of the plating bath(s) or subsequent surface finishing operations.
3. Comparable product quality is achieved with each comparison of conventional processing and the Picklex® alternative process.
4. The following chemical costs are used:
   - Hydrochloric acid, 37% HCl, $72/ton
   - Sodium hydroxide, USP pellets, $1.70/lb
   - Alumiprep® 33, as used, $10/gallon (Henkel Surface Technologies, 2000)
   - Chromate conversion coating, $10/gallon (Henkel Surface Technologies, 2000)
   - Picklex® as used, $40/gallon (ICP, 2000)
5. The chemical consumption and make-up rates are as follows: Alkali cleaner is replaced every 6 months (2,500 lb NaOH/yr); Picklex® is replaced every 12 months (500 gal/yr); pickling solution is replaced every 6 months (10,000 lb HCl/yr); rust remover is replaced every 6 months (10,000 lb/yr); Alumiprep® 33 is replaced every 6 months (1,000 gal/yr).
6. Use of Picklex® solution can replace both the alkali cleaning and the chromate conversion coating in the surface preparation of aluminum for powder coating applications.
7. Waste disposal cost of replacing the chemical baths to averages $0.50/lb.
8. Only one operator is needed for each line.
9. Operator’s wage is $20/hour.
10. Workload is consistent throughout year.

Chromate Conversion Coating on Aluminum

Figure 2 illustrates the sequential process steps for both conventional chromate conversion coating on aluminum and the alternative Picklex® process. As shown, the use of Picklex® (Al-P-R-N-N-PC) replaces both the pretreatment (alkali cleaning, 2 rinse steps, etch, 3 rinse steps, deoxidizer, 2 rinse steps) and chromate conversion coating (chromate conversion coat and three rinse steps).

The revised capital cost savings associated with eliminating these process steps and associated equipment are estimated to be $254,000 because of the decreased number of process steps.

Using the same factored cost estimate of Phase I that includes piping, installation, electrical, instrumentation and controls, utilities and other services the cost savings was calculated. Table 8 provides detailed cost elements that were estimated in the engineering assessment.

- **Table 8. Capital Cost Savings**

Cost Element	Commercial Pretreatment and Chromate Conversion Coating on Aluminum	Commercial Pretreatment and Zinc Phosphatizing on Steel
Tank	$27,000	$15,000
Spill Containment	$1,500	$750
Pump	$26,000	$26,000
Filter	$7,200	$7,200
Mixer	0	0
Heater	$8,000	$6,000
Power Supply	0	$8,000
Subtotal PEC	$69,700	$62,950
Installation (30% PEC)	$21,000	$19,000
Piping (30% PEC)	$21,000	$19,000
Instrumentation (10% PEC)	$7,000	$6,300
Electrical (10% PEC)	$7,000	$6,300
Utilities		
Engineering (33% PEC)	$23,000	$21,000
Contingency (50% PEC)	$35,000	$32,000
Working Capital		
Total Capital Savings	$254,000	$230,000

Empty cells indicate cost element was not estimated.
PEC = purchased equipment cost.

Additional savings are not included for incremental cost of building/floor space, water treatment, and ventilation. These additional savings could be significant for a new facility (Greenfield site) or a total facility refurbishment that included these ancillary components, especially if the freed-up space enabled additional production capacity to be brought on line.

Overall, the operating costs for conventional pretreatment of aluminum are $46,000 higher than the alternative Picklex® process. Table 9 presents the estimated operating cost savings, including the direct labor costs based on the process time needed at Mills. The assumptions included only one operator is needed, the hourly wage is $20, and the workload is consistent throughout the year. The process time not including degreasing, drying, and powder coating (times are the same for both commercial and Picklex® processes) is 20 minutes for pretreatment and chromate conversion coating on aluminum and 1 minute for processing with Picklex® as the pretreatment and conversion coat. The chemical costs remained the same as Phase I. Consistent with Phase I, both conversion coating processes would have the same powder top coating operations and costs.

Zinc Phosphatizing on Steel

Figure 1 illustrates the process steps for both conventional zinc phosphatizing on steel and the Picklex® process. The use of Picklex® replaces the pretreatment (electro cleaner and one rinse step) and conversion coating (conversion coat and three rinses).

The capital cost savings, shown in Table 8 is estimated to be $ 230,000 using the same factored cost estimate as Phase I which includes piping, installation, electrical, instrumentation and controls, utilities, and other services. The revised capital cost savings results from the reduced number of steps between Mills' process and the Picklex® alternative.

As previously stated, additional savings are not included for incremental cost of building/floor space, water treatment, and ventilation.

The operating cost savings, presented in Table 9 include the direct labor costs. Using the assumptions described in the chromate conversion cost estimate, the direct labor costs for using zinc phosphate are $36,600 higher than using Picklex®. The estimated time for processing one load through the zinc phosphate line is 25 minutes compared to the 2 minutes process time for Picklex® with steel.

▪ Table 9. Operating Cost Estimate

Cost Element	Unit Cost	Conventional Process		Picklex® Process	
Chromate Conversion Coating on Aluminum					
Alkali Cleaner	$1.70/lb	2,500 lb	$4,250/yr		
Alumiprep® 33	$10/gal	1,000 gal	$10,000/yr		
Chromate Conversion Coating	$10/gal	1,000 gal	$10,000/yr		
DI Water	$0.05/gal	10,000 gal	$500/yr	500 gal	$25/yr
Picklex®	$40/gal			500 gal	$20,000/yr
Waste Treatment	$0.50/lb	12,000 lb	$6,000/yr	5,000 lb	$2,500/yr
Direct Labor	$20/hr	2000 hr	$40,000/yr	100 hr	$2,000/yr
Maintenance					
Operating Supplies					
Utilities					
Analytical Lab					
Fixed Costs					
Indirect Costs (OH)					
Subtotal			$70,750/yr		$24,525/yr
Indirect Costs (OH)					
Subtotal			$70,750/yr		$24,525/yr
Chemicals		Quantity	Annual Cost	Quantity	Annual Cost
Zinc Phosphatizing on Steel					
Aeroclean DN 30	$4.91/gal	1,000 gal/yr	$4910/yr		
HCl	$72/ton	5 ton/yr	$360/yr		
Aerocote #3	$7.05/gal	1,000 gal/yr	$7050/yr		
DI Water	$0.05/gal	10,000 gal	$500/yr	500 gal	$25/yr
Picklex®	$40/gal			500 gal	$20,000/yr
Waste Treatment	$0.50/lb	10,000 lb	$5,000/yr	5,000 lb	$2,500/yr
Direct Labor	$20/hr	2000 hr	$40,000/yr	170 hr	$3400/yr
Maintenance					
Operating Supplies					
Utilities					
Analytical Lab					
Fixed Costs					
Indirect Costs (OH)					
Subtotal			$58,000/yr		$26,000/yr

Empty cells indicate that cost element does not exist.

Results and Discussion

Several qualitative processing advantages of Picklex® were found during Phase I, which include adequate draining time, easy agitation, and slow evaporation rate. An extended bath use period test was performed during Phase I, which showed that the bath did not form solids with use, and that Picklex® operates at ambient temperature. These advantages of Picklex® were confirmed during Phase II.

The field testing at Mills showed that the use of Picklex® reduced the number of process steps considerably compared to commercial processes. The optimum Picklex® process for aluminum and steel that receives a powder coat finish may consist of degreasing, Picklex® immersion dip (30 seconds for aluminum and 90 seconds for steel), and a quick rinse step (in and out). Then the processed parts may be dried and powder coated. The commercial processes for both pretreatment and chromate conversion coating for aluminum and pretreatment and zinc phosphate conversion coat on steel include many more process steps (11 more steps for aluminum and 5 more steps for steel).

A disadvantage of Picklex® is that the near term unit cost is $40/gallon; however the remaining operating and capital cost savings may offset the difference in chemical costs. Also Picklex® has a slow evaporation rate and high tolerance to contamination and so does not need to be replaced on a regular basis.

The revised engineering assessment showed the economic impact of using Picklex® as a replacement for chromate conversion coating and zinc phosphatizing. Both the capital cost savings and the annual operating cost savings are summarized in Table 10.

Table 10. Summary of Cost Reductions of Using Picklex®
Instead of Conventional Pretreatments

Cost Reduction	Savings Relative to CCC on Aluminum	Zinc Phosphatizing on Steel
Capital Cost Savings	$254,000	$230,000
Annual Operating Cost Savings	$ 46,000	$ 36,600

Recommendations

Steel and aluminum components were evaluated during Phase II. The Picklex® treated aluminum components provided improved adhesion over the current production technique. Based on the positive test results, an application specific field test on aluminum components is recommended.

References

Battelle, 2000, *Picklex® Field Test Plan*. Prepared for U.S. EPA's NRMRL. June 5, 2000.

Carpenter, S. 1999. "One-Step, Zero-Effluent Organic Phosphating." *Metal Finishing* September): 56.

Ferguson, D., Chen, A., Hindin, B., Monzyk, B "Picklex ® as a Non-Polluting Metal Surface Finishing Pretreatment and Pretreatment/Conversion Coating ", *Clean Products and Processes* Volume 2, Number 4, February 2001.

Ferguson, D., Chen, A., Hindin, B., Monzyk, B. „Use of Picklex® as a Cost Effective Metal Treatment“,Report on Contract No. 68-C7-0008 to Battelle, accepted for publication (Ferguson, 2000).

Q-Panel Laboratory Products. 1999. Reference: 3105 Al and C1010 Steel are in most common use in the manufacturing of commercial products such as home appliances and automobiles.

United States Environmental Protection Agency. 1995. *Toxic Release Inventory (TRI) Release Data for Fabricated Metals Facilities (S34).*

United States Environmental Protection Agency. 1999. Update of 1995 document, *Title 40: Environmental Protection Code of Federal Regulations*. Available at: www.epa.gov/docs/epacfr40/chapt-I.info/subch-I/40P0261.pdf.